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(54) A non-aqueous electrolyte type secondary battery

(57) A non-aqueous electrolyte secondary cell having a negative electrode, a positive electrode and a non-aqueous electrolytic solution, in which a carbonaceous material is used as an active negative-electrode material, is disclosed. The negative electrode is constituted by a carbon sintered mass obtained on sintering the carbonaceous material or a carbon sintered mass-current collector composite material. The secondary cell is improved in the amount of the active material packed in the negative electrode, energy density and in the charging/discharging efficiency. If the carbon sintered mass-current collector composite material is employed for the negative electrode, further improvement in the electrical conductivity and charging/discharging efficiency in the negative electrode is achieved.

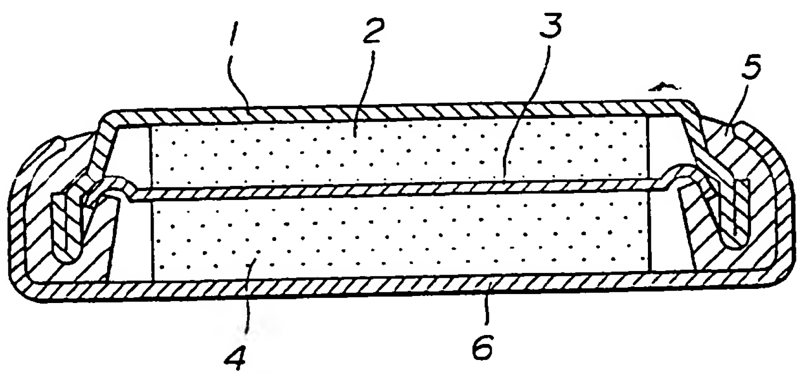

FIG.1

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Description

BACKGROUND OF THE INVENTION

This invention relates to a non-aqueous electrolyte secondary cell and, more particularly, to a non-aqueous electrolyte secondary cell employing a carbonaceous material for its negative electrode.

Recently, in keeping up with the propagation of portable equipment, such as a video camera or an audio cassette, there is an increasing demand for a secondary cell, which is usable repeatedly, to take the place of a primary cell, which is disposable.

Most of the secondary cells, now in use, are nickel-cadmium cells employing an alkaline electrolyte solution. The secondary cell however has a voltage of approximately 1.2 V such that it is difficult to raise the energy density. In addition, the secondary cell has a defect that it has a high self-discharge rate at ambient temperature of not less than 20% per month.

Fore this reason, investigations on a non-aqueous electrolyte secondary cell employing a non-aqueous solution as an electrolyte and light metal such as lithium for a negative electrode are proceeding. This non-aqueous electrolyte secondary cell has a high voltage of 3 V and hence a high energy density so that it has such advantages as low self-discharge rate and lightness of weight. However, if the non-aqueous electrolyte secondary cell employing lithium for its negative electrode is charged and discharged repeatedly, metal lithium tends to undergo dendritic crystal growth from the negative electrode until it contacts with the positive electrode. The result is shorting in the inside of the cell thus leading to difficulties in practical utilization of the cell.

In this consideration, investigations on a non-aqueous electrolyte secondary cell in which lithium is alloyed with other metals and the resulting alloy is used for the negative electrode are also proceeding. However, such cell has a defect that, if the cell is charged and discharged repeatedly, the alloy constituting the negative electrode tends to be comminuted is size, thus again leading to difficulties in practical utilization of the cell.

There is also proposed a non-aqueous electrolyte secondary cell employing a carbonaceous material, such as coke, as an active negative electrode material. This non-aqueous electrolyte secondary cell, exploiting doping/undoping of lithium ions to and from the spacing between carbon layers, is not susceptible to precipitation of metal lithium nor to alloy comminution, contrary to the case of employing metal lithium or lithium alloy as the active negative electrode material. The result is optimum cyclic characteristics of the cell. If a lithium/transition metal composite oxide represented by Li_xMO_2, where M denotes one or more transition metals and x is such that $0.05 \leq x \leq 1.10$, as an active positive electrode material, as disclosed in JP Patent Kokai Publication JP-A-63-135099 (1988) or JP Patent Kokai Publication JP-A-1-304664 (1989), the cell capacity may be improved, such that it becomes possible to produce a non-aqueous electrolyte secondary cell having high energy density.

However, as compared to the non-aqueous electrolyte secondary cell employing metal lithium or the like as the active negative electrode material, the non-aqueous electrolyte secondary cell, employing the carbonaceous material as the active negative electrode material, is inferior in energy density, although it id superior in cyclic service life and safety.

One of the reasons therefor is that, if the carbonaceous material is employed as the active negative electrode material, powders of the carbonaceous material are usually kneaded with a binder or a dispersant to form a slurry, which is then coated on a current-collector or is directly molded to form a negative electrode, so that the active material is decreased in an amount corresponding to the binder content. In this case, the binder which does not contribute to the cell capacity accounts for 10 to 20% of the negative electrode.

Although it is contemplated to improve the packing density of the carbonaceous material to obviate such deficiency, it cannot be raised beyond a certain limit value, thus impeding further increase in the energy density.

OBJECT AND SUMMARY OF THE INVENTION

In view of the foregoing, it is a principal object of the present invention to provide a non-aqueous electrolyte secondary cell whereby a high energy density may be realized while the advantage derived from the use of the carbonaceous material as an active negative electrode material is maintained.

For accomplishing the object, the present inventors have conducted eager researches and arrived at an information that an agglomerated carbon sintered mass can be obtained on sintering a specific carbonaceous material and a negative electrode having a high packing amount of an active material can be obtained using this carbon sintered mass without employing a binder.

The present invention, completed based upon this information, resides in a non-aqueous electrolyte secondary cell having a negative electrode containing a carbonaceous material as an active negative-electrode material, a positive electrode and a non-aqueous electrolytic solution, wherein the negative electrode is formed of a carbon sintered mass obtained on sintering the carbonac ous material.

The negative electrode is made up of a carbon sintered mass obtained on sintering a carbonaceous material and a current collector.

The present invention is applied to a non-aqueous electrolyte secondary cell having a negative electrode formed of the carbonaceous material as the active negative material, a positive electrode and a non-aqueous electrolytic solution. According to the present invention, the negative electrode of the non-aqueous electrolyte secondary cell is formed of a carbon sintered mass obtained on sintering the carbonaceous material.

If the carbonaceous material is employed as an active negative electrode material, the conventional practice has been to knead powders of the carbonaceous material with a binder to from a mixture for the negative electrode which is then formed to a desired electrode shape or held by a current collector to constitute the negative electrode. Such electrode is lowered in the packing density of the active negative electrode material in an amount corresponding to the amount of the binder employed, such that the energy density of the cell cannot be raised sufficiently.

On the other hand, if the negative electrode is constituted by the carbon sintered mass obtained on directly sintering the carbonaceous material, the packing density of the active negative electrode material is increased in an amount corresponding to the amount of the binder which is now not used, as a result of which a negative electrode having a larger reaction area may be produced. In addition, sintering leads to improved electrical conductivity of the carbonaceous material, thus allowing to lower the internal resistance of the cell as compared to the case of employing a non-sintered carbonaceous material. Thus the use of such negative electrode leads to improved energy density and improved charging/discharging efficiency of the cell.

The above-mentioned carbon sintered mass can be produced on compression molding of a starting carbonaceous material to the shape of a desired electrode and subsequently sintering the molded mass in an inert gas at a pre-set temperature.

As the starting carbonaceous material, such carbonaceous material as contains an amount of resin components, such as petroleum pitch, binder pitch, high molecular resin or green coke, is employed. Alternatively, graphite, thermally cracked carbons, cokes, such as petroleum coke, pitch coke or coal coke, carbon black, such as acetylene black, vitreous carbon, sintered organic high molecular materials, that is organic high molecular materials sintered in an inert gas stream or in vacuum at a suitable temperature such as at 500°c or higher, or carbon fibers, may be mixed with the aforementioned resin-containing pitches, resins exhibiting high sinterability, such as furan resin, divinylbenzene or polyvinylidene fluoride, to give a starting mixture, which is sintered. The resin content in the starting material is carbonized or volatilized off on sintering to give a carbon sintered mass free of the resin content.

The volume density of the sintered mass is preferably 0.8 to 1.95 g/ml. If the volume density is outside the above range, the energy density of the cell cannot be increased sufficiently.

The negative electrode may be constituted by such carbon sintered mass carried by a current collector. The current collector, if used, leads to improved electrical conductivity of the negative electrode, as a result of which the internal resistance of the cell is lowered to suppress polarization during charging/discharging. The negative electrode carried by the current collector of the negative electrode may be obtained by inserting a current collector in the starting carbonaceous material before compression molding, and by carrying out the compression molding and sintering in this state.

Preferably, the current collector is of a material boiling at a temperature higher than 1000°C and difficult to alloy with lithium, in order that, since the current collector is placed under a sintering atmosphere reaching 1000°C, it is not melted at such high temperature. Such material may be enumerated by copper, nickel, cobalt, iron, chromium, molybdenum, tantalum, tungsten, stainless steel, titanium and mixtures thereof. Above all, copper, nickel, stainless steel, iron or alloys thereof is most preferred.

The melting points of these metals are shown in Table 1.

TABLE 1

Name of Substances	Melting Point (°C)
copper	1083
nickel	1455
cobalt	1492
iron	1535
chromium	1905
molybdenum	2622
tantalum	2850
tungsten	3382
stainless steel	1427 - 1471
titanium	1820

Since the current collector occupies a small area, it is preferably a foil, mesh, expanded metal or punched metal provided with pores capable of transmitting ions therethrough.

According to the present invention, the carbon sintered mass is employed as the negative electrode. On the other hand, the materials usually employed for this sort of the cell may be employed as the materials for the positive electrode and the electrolytic solution.

As an active positive electrode material, a compound represented by Li_xMO_2, where M denotes one or more transition metals, preferably at least one of Co, Ni or Fe, with $0.05 \leq x \leq 1.10$, is employed. Such active material may be enumerated by composite oxides such as $LiCoO_2$, $LiNiO_2$ and $LiNi_yCo_{(1-y)}O_2$, where x and y are such that $0.05 \leq x \leq 1.10$ and $0 < y < 1$, and $LiMn_2O_4$.

The composite oxides may be obtained on mixing carbonates of lithium, cobalt or nickel, depending on the composition, and subsequently sintering the mixture in an oxygen atmosphere at a temperature of from 600° to 1000°C. The starting material is not limited to the carbonates and the composite oxides may also be synthesized from hydroxides or oxides.

The electrolyte solution hitherto known may be employed, provided that the solution is an electrolyte dissolved in an organic solvent.

The organic solvents may be enumerated by esters, such as propylene carbonate, ethylene carbonate or γ-butyrolactone, ethers, such as diethylether, tetrahydrofuran, substituted tetrahydrofuran, dioxorane, pyrane, derivatives thereof, dimethoxyethane or diethoxyethane, 3-substituted 2-oxazolidinones, such as 3-methyl- 2-oxazolidinone, sulforane, methylsulforane, acetonitrile and propionitrile. These may be used alone or as a mixture.

The electrolytes may be enumerated by lithium perhydrochlorate, lithium boron fluoride, lithium phosphorus fluoride, lithium chloride aluminate, lithium halogenides, trifluoromethane and lithium solfonate.

The shape of the cell according to the present invention may be a card shape or a square shape employing layered electrodes, such that it is not limited to the so-called coin or button shape.

With the non-aqueous electrolyte secondary cell according to the present invention, the carbon sintered mass, obtained on sintering a carbonaceous material, is employed as a negative electrode material.

As compared to the negative electrode formed of a negative electrode mixture of powders of the carbonaceous materials and the binder, the negative electrode formed of the carbon sintered mass is improved in the packing density of the active material by a value corresponding to the amount of the binder which is not in use, thus giving a larger reaction area. In addition, sintering leads to increased electrically conductivity of the carbonaceous material to decrease the internal resistance of the cell than in the case of using a non-sintered carbonaceous material, thus improving the energy density and charging/discharging efficiency of the cell.

If the current collector is unified to the carbon sintered mass, the negative electrode is improved in electrical conductivity, thus further improving the charging/discharging efficiency.

With the non-aqueous electrolyte secondary cell of the present invention, since the negative electrode is constituted by a carbon sintered mass obtained on sintering the carbonaceous material, or a carbon sintered mass- current collector composite material, the secondary cell is improved in the amount of the active material packed in the n gative electrode, energy density and in the charging/discharging efficiency. If, above all, the carbon sintered mass- current collector composite material is employed for the negative electrode, further improvement in the electrical conductivity and in the

charging/discharging efficiency of the negative electrode may be achieved, thus contributing to the propagation of the portable electronic equipment employing secondary cells.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a schematic cross-sectional view showing an embodiment of a coin-shaped cell according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be explained with reference to illustrative Examples applied to a coin-shaped cell, based upon experimental results.

Example 1-1

A coin-shaped cell was produced in the present Example as shown in Fig.1. In the present Example, such coin-shaped cell was produced in the following manner.

First, for producing a positive-electrode pellet 4, lithium carbonate and cobalt carbonate were mixed together at a molar ratio of 0.5:1 and sintered in air for five hours at a temperature of 900°C to produce agglomerated $LiCoO_2$ which then was ball-milled and sieved to produce an active positive electrode material having a mean particle size or mean volumetric particle diameter of 10 µm.

91 parts by weight of this active positive electrode material, 6 parts by weight of graphite, as an electrically conductive material, and 3 parts by weight of polyvinylidene fluoride, as a binder, were mixed together. To the resulting mixture was further added N-methyl-pyrrolidone as a dispersant to prepare a positive-electrode paste. This positive-electrode paste was dried and molded to a disc shape 15.5 mm in diameter to prepare a positive-electrode pellet 4.

Then, for preparing a negative-electrode sintered mass 2, a binder pitch manufactured by OSAKA KASEI CO. LTD. under the trade name of TGP 3000 was pelletized to a disc shape 16.5 mm in diameter and compression molded under a pressure of 1 t. The molded product was sintered at a temperature of 1000°C for three hours to produce a disc-shaped negative-electrode sintered mass 2 which was 16.00 mm in diameter. The volume density d of the sintered mass was 0.8 g/ml.

An electrolytic solution was prepared by dissolving $LiPF_6$ in a mixed liquid of ethylene carbonate and diethyl carbonate at a concentration of 1 mol/liter.

The positive-electrode pellet 4 and the negative-electrode sintered mass 2 were then housed in a positive-electrode can 6 and a negative-electrode cup 1, respectively, and were layered via a thin-film separator 3 of polypropylene in-between. The electrolytic solution was charged into the can which was caulked via a gasket 5 to produce a coin-shaped cell 20 mm in diameter and 2.5 mm in thickness.

Example 1-2

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative-electrode sintered mass in the following manner.

That is, the binder pitch TGP 3000 was pelletized to a disc shape 16.5 mm in diameter and compression molded at a pressure of 2 t. The molded product was sintered in an inert gas for three hours at a temperature of 1000°C to produce a negative-electrode disc-shaped sintered molded product 16.0 mm in diameter. The volume density of the sintered mass was 1.0 g/ml.

Example 1-3

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative electrode sintered mass in the following manner.

That is, the binder pitch TGP 3000 was pelletized to a disc shape 16.5 mm in diameter and compression molded at a pressure of 3 t. The molded product was sintered in an inert gas for three hours at a temperature of 1000°C to produce a negative-electrode sintered disc-shaped molded product 16.0 mm in diameter. The volume density of the sintered mass was 1.2 g/ml.

Example 1-4

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative-electrode sintered mass in the following manner.

That is, the binder pitch TGP 3000 was pelletized to a disc shape 16.5 mm in diamet r and compression molded at a pressure of 4 t. The molded product was sintered in an inert gas for three hours at a temperature of 1000°C to produce a negative-electrode sintered disc-shaped molded product 16.0 mm in diameter. The volume density of the sintered mass was 1.4 g/ml.

Example 1-5

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative-electrode sintered mass in the following manner.

That is, the binder pitch TGP 3000 was pelletized to a disc shape 16.5 mm in diameter and compression molded at a pressure of 5 t. The molded product was sintered in an inert gas for three hours at a temperature of 1000°C to produce a negative-electrode sintered disc-shaped molded product 16.0 mm in diameter. The volume density of the sintered mass was 1.8 g/ml.

Example 1-6

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative-electrode sintered mass in the following manner.

That is, the binder pitch TGP 3000 was pelletized to a disc shape 16.5 mm in diameter and compression molded at a pressure of 10 t. The molded product was sintered in an inert gas for three hours at a temperature of 1000°C to produce a negative-electrode sintered disc-shaped molded product 16.0 mm in diameter. The volume density of the sintered mass was 1.95 g/ml.

Example 1-7

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative-electrode sintered mass in the following manner.

First, the pitch coke was pulverized for 15 minutes to powders in a vibration mill containing stainless steel balls 12.7 mm in diameter. The true density of the pitch coke was 2.03 g/cm^3, while the spacing of the (002) plane as found by X-ray diffraction pursuant to the Law for the Japan Society for the Promotion of Science was 3.46 Å and the crystal thickness along the C-axis Lc was 40 Å. The mean particle size was 33 µm.

50 wt% of powders of the pitch coke and 50 wt% of the binder pitch TGP 3000 were weighed out and mixed together in a mortar. The mixture was pelletized to a disc-shaped pellet 16 mm in diameter and compression molded at a pressure of 3 t. The molded product was sintered in an inert gas at 1000°C for three hours to give a disc-shaped negative-electrode sintered mass 16 mm in diameter. The volume density d of the sintered mass was 1.2 g/ml.

Example 1-8

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative-electrode sintered mass in the following manner.

50 wt% of graphite, manufactured by LONZA INC. under the trade name of KS-15 and 50 wt% of the binder pitch TGP 3000 were weighed out and mixed together in a mortar. The resulting mixture was pelletized to a disc-shaped pellet 16.5 mm in diameter and compression molded at a pressure of 3 t. The molded product was sintered in an inert gas at 1000°C for three hours to give a disc-shaped negative-electrode sintered molded product 16 mm in diameter. The volume density d of the sintered molded product was 1.5 g/ml.

Comparative Example 1-1

A coin-shaped cell was prepared in the same way as in Example 1-1 except preparing a negative electrode in the following manner.

90 parts by weight of powders of the pitch coke, which were the same as those employed in Example 1-7, and 10 parts by weight of polyvinylidene chloride as a binder, were mixed together. To the resulting mixture was added N-methyl-pyrrolidone as a dispersant to prepare a paste, which was then dried and compression molded to a disc 16 mm in diameter to prepare a negative-electrode pellet 2.

The internal resistance, charging capacity and the discharging capacity were measured of the cells of the Examples 1-1 to 1-8 and the Comparative Example 1-1 prepared as described above.

Th charging and discharging were carried out under a condition that constant-current charging was carried out under the conditions of a charging current of 1 mA and a terminal voltage of 4.2 V after which constant current discharging was carried out under the conditions of a discharging current of 1 mA and a terminal voltage of 3.0 V. The results are

shown in Table 2.

TABLE 2

	Binder Quantity %	Negative Electrode Density g/ml	Cell Internal Resistance Ω	Charging Capacity mAh	Discharging Capacity mAh	Charging/Discharging Efficiency %
Comp. Ex.1-1	10	1.0	15	57	43	75
Ex.1-1	0	0.8	6	58	53	92
Ex.1-2	0	1.0	8	66	60	90
Ex.1-3	0	1.2	9	79	71	90
Ex.1-4	0	1.4	10	92	79	85
Ex.1-5	0	1.8	10	119	98	82
Ex.1-6	0	1.95	10	129	103	80
Ex.1-7	0	1.2	8	72	67	92
Ex.1-8	0	1.5	5	99	94	95

It is seen from Table 2 that, as compared to the cell of the Comparative Example 1-1 containing the binder in its negative electrode, the cells of Examples 1-1 to 1-8 employing the carbon sintered mass for negative electrodes thereof are higher in the negative electrode density and superior in the charging/discharging efficiency. The internal resistance of the cells of the Examples 1-1 to 1-8 are also lower. Above al, with the cells of the Examples 1-7 and 1-8, in which the carbon sintered mass is produced from the mixture of the binder pitch with the pitch coke and the mixture of the pitch coke and graphite, respectively, the charging/discharging efficiency shows extremely high values of 92% and 95%, respectively.

For checking an upper limit of the volume density of the negative-electrode sintered mass, sintering was carried out under the same conditions as those of Example 1 except setting the molding pressure of the binder pitch to 20 t to produce a negative-electrode sintered mass having a volume density of 2.0 g/ml. The sintered mass, thus produced, was built into a coin-shaped cell. The internal resistance, charging capacity, discharging capacity and the charging/discharging capacity of the cell were found to be 20 ohm, 132 mAh, 40 mAh and 30%, respectively. These characteristics are inferior as compared to those of the cell of the Comparative Example 1-1. It is seen from this that the volume density of the negative-electrode sintered mass which is simply higher is not satisfactory and that it is necessary to prescribe the range of the volume density to e.g., 0.8 to 1.95 g/ml.

Example 2-1

A coin-shaped cell was prepared in the same way as in Example 1-1 except that a composite sintered mass of a carbon sintered mass and a carbon collector produced in a manner now to be described was employed for a negative electrode.

A special binder pitch manufactured by OSAKA KASEI CO. LTD. under the trade name of LEC-1 was temporarily sintered in an inert gas at 900°C for one hour to a temporarily sintered mass (pitch coke) which was then pulverized to a particle size not more than 25 mesh size. This temporarily sintered mass (pitch coke) and an unsintered special binder LEC-1 were mixed at a ratio of 1:1 to give a powder mixture which was then temporarily molded to a pellet shape. Into a mid part of the powder mixture was inserted copper expanded metal and the resulting mass was compression molded under a pressure of 3 t to a pellet 16.5 mm in diameter. The copper expanded metal was 0.1 mm in thickness with a pore being 1 X 2 mm in shape and with the pore ratio being 50%.

The molded product was sintered in an inert gas at 1000°C for three hours to produce a sintered composite product of the carbon sintered body and the current collector. The composite product was 16.0 mm in diameter. The volume density d of the carbonaceous portion of the sintered composite product, excluding the current collector portion, was 1.2 g/ml.

Example 2-2

A coin-shaped cell was prepared in the same way as in Example 2-1, except that, for producing a carbon sintered body-current collector composite disc-shaped product, a copper foil 0.1 mm thick was used as a current collector and

applied to a lateral surface of the carbon sintered mass for compositization. The volume density d of the carbonaceous portion of the sintered composite product, excluding the current collector portion, was 1.2 g/ml.

Example 2-3

A coin-shaped cell was prepared in the same way as in Example 2-1, except that, for producing a carbon sintered body-current collector composite disc-shaped product, punching metal with a pore ratio of 50%, a thickness of 0.1 mm and a pore diameter of 1 mm was used as a current collector. The volume density d of the carbonaceous portion of the sintered composite product, excluding the current collector portion, was 1.2 g/ml.

Example 2-4

A coin-shaped cell was prepared in the same way as in Example 2-1, except that, for producing a carbon sintered body-current collector composite disc-shaped product, nickel expanded metal with a pore ratio of 50% was used as a current collector. The volume density d of the carbonaceous portion of the sintered composite product, excluding the current collector portion, was 1.2 g/ml.

Example 2-5

A coin-shaped cell was prepared in the same way as in Example 2-1, except that, for producing a carbon sintered body-current collector composite disc-shaped product, stainless steel 304 expanded metal with a pore ratio of 50% was used as a current collector. The volume density d of the carbonaceous portion of the sintered composite product, excluding the current collector portion, was 1.2 g/ml.

Comparative Example 2-1

A coin-shaped cell was prepared in the same way as in Example 1-1, except that a pellet of a negative electrode mixture and a current collector bonded to each other under pressure were employed for a negative electrode. The pellet of the negative electrode mixture and the current collector bonded to each other under pressure were prepared by attaching the current collector to a pellet formed of the negative electrode mixture in the following manner.

That is, 90 parts by weight of pitch coke powders, which were the same as those employed in Example 1-7, and 10 parts by weight of polyvinylidene fluoride, as a binder, were mixed together to prepare a negative electrode mixture to which N-methylpyrrolidone was added as a dispersant to give a paste of the negative electrode mixture. This paste was dried to a pellet 16.0 mm in diameter and pressed against and bonded to a copper expanded metal as a current collector to produce a negative electrode.

The internal resistance, charging capacity, discharging capacity and the charging/discharging efficiency of the coin-shaped cells of the Examples 2-1 to 2-5 and the Comparative Example 2-1, thus produced, were measured. The charging and discharging were carried out under a condition that constant-current charging was carried out at a charging current of 1 mA and a terminal voltage of 4.2 V, after which constant current discharging was carried out at a discharging current of 5 mA and at up to a terminal voltage of 3.0 V. The results are shown in Table 2. For comparison, similar measurements were made of the cells of Comparative Example 2-2 in which only the carbon sintered mass with a volume density of 1.2 g/ml was used for the negative electrode without employing a current collector. The results are also shown in Table 3.

TABLE 3

	Binder Quantity %	Metal Current Collector	Negative Electrode Density g/ml	Cell Internal Resistance Ω	Charging Capacity mAh	Discharging Capacity mAh	Charging/Discharging Efficiency %
Comp. Ex.2-1	10	Yes	1.0	15	57	43	75
Comp. Ex.2-2	0	No	1.2	12	66	53	80
Ex.2-1	0	Yes	1.2	6	66	61	92
Ex.2-2	0	Yes	1.2	8	66	60	91
Ex.2-3	0	Yes	1.2	7	66	60	91
Ex.2-4	0	Yes	1.2	8	66	60	91
Ex.2-5	0	Yes	1.2	9	66	60	91

As compared to a cell of Comparative Example 2-1 in which a pellet of a negative electrode mixture of the carbonaceous material and the binder on one hand and the current collector on the other hand are bonded under pressure to each other so as to be used for its negative electrode, or a cell of Examples 1 to 3 in which only the carbon sintered mass is used for its negative electrode, the cells of Examples 2-1 to 2-5, in which a sintered composite product of the carbon sintered mass and the current collector is employed for a negative electrode, is high in charging capacity and discharging capacity and superior in charging/discharging efficiency, as shown in Table 3. This is possibly due to the fact that the reaction area is increased by not employing the binder as the negative electrode, and that the negative electrode is improved in electrical conductivity by unifying the metal current conductor to the carbonaceous material by sintering, as a result of which the internal resistance of the cell is decreased and the polarization during charging/discharging is diminished.

It is seen from this that the carbon sintered mass combined with the current collector leads to further improvement of the performance of the cell.

Although the foregoing descriptio has been made of a coin-shaped cell, the present invention may also be applied to a system employing a layered electrode with similar favorable effects. Thus the technique disclosed herein is highly effective when applied to a square-shaped cell or a card type cell. In addition, similar effects to those produced with the use of the special binder pitch LEC-1 may naturally be produced with the use of carbonaceous materials other than the special binder pitch LEC-1.

Claims

1. A non-aqueous electrolyte secondary cell having a negative electrode containing a carbonaceous material as an active negative-terminal material, a positive electrode and a non-aqueous electrolytic solution, wherein the improvement resides in that said negative electrode is formed only of a carbon sintered mass obtained on sintering the carbonaceous material.

2. The non-aqueous electrolyte secondary cell as claimed in claim 1, wherein said negative electrode is made up of the carbon sintered mass obtained on sintering the carbonaceous material and a current collector.

3. The non-aqueous electrolyte secondary cell as claimed in claim 2, wherein said current collector is formed of metal or an alloy melting at 1000°C or higher.

4. The non-aqueous electrolyte secondary cell as claimed in claim 3, wherein said current collector is formed of copper, nickel, stainless steel, iron or mixtures thereof.

5. The non-aqueous electrolyte secondary cell as claimed in claim 3, wherein said current collector is in the form of a metal sheet having numerous pores.

6. The non-aqueous electrolyte secondary cell as claimed in claim 5, wherein said current collector is in the form of a mesh, expanded metal or a punching metal.

7. The non-aqueous electrolyte secondary cell as claimed in claim 1, wherein said carbon sintered mass has a volume density of 0.8 to 1.95/ml.

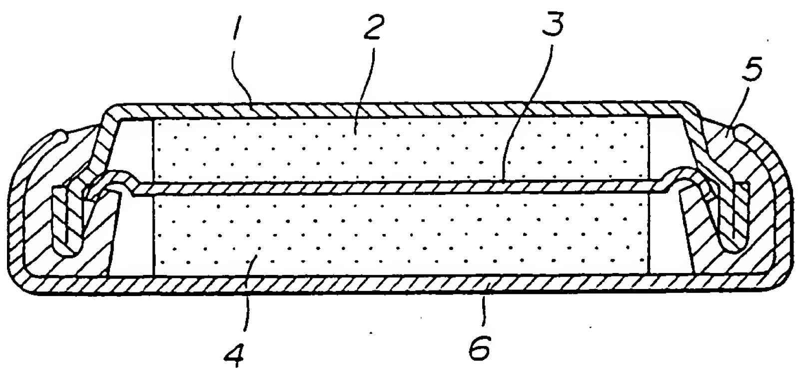

FIG.1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 0093

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 527 054 (MITSUBISHI) * column 17, line 36 - line 40; claim 1 * ---	1-7	H01M4/58
A	EP-A-0 309 171 (SHARP) * column 2, line 16 - line 17; claim 1 * -----	1,3-6	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
H01M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 October 1995	Andrews, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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